Synopsis

Ph.D. in Chemistry

Synthesis, Characterization and Electrochemical Studies of Biomass Derived Carbon Materials from Leaves of *Madhuca longifolia* and *Mimusops elengi* for Supercapacitor Electrode Applications.

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Introduction

An energy storage device is used for storing electric energy when needed and releasing it energy when required. As a measure to counter global warming, the role of energy storage device technology in field such as renewable energy generation and highly automobile system will become increasingly important.

Supercapacitor also known as Ultra capacitors and Electrochemical Double Layer Capacitor (EDLC) fills the energy gap between batteries and conventional capacitors. Supercapacitor has emerged as new technology in energy storage. It has same fundamental equation as that of conventional capacitor. Supercapacitors are classified into two types based on their charge storage mechanism. They are electric double layer capacitors (EDLCs) and Pseudocapacitors. (Karnan et al. 2016)

Supercapacitor is constructed from two carbon-based electrodes, separator between electrodes and electrolyte. It stores charge at interface between high surface electrode and liquid electrolyte. Charge separation is created nearly at each solid- liquid interference. It is observed in super capacitor, that distance between electrodes is angstroms and area is thousands of square meters per gram of electrode. Supercapacitors combine the properties of capacitors and batteries into one device

Biomass is commonly used to refer to plant materials in the term of energy context but it also refers by products and waste from animal husbandry, food processing and residential organic wastes. Biomass is made up of a mixture of organic molecules including hydrogen, oxygen, and nitrogen with higher quantity of carbon. The development of carbon materials which will be applicable in wide sectors are the growing research. These carbon materials can be easily obtained from the environment and biomass-based industry.

The carbon materials derived from various biomass precursors have placed remarkable results in various applications. They are used as electrode in supercapacitors, dye sensitized solar cell, catalyst, oxygen reduction reactions, oil water separation, anode material in sodium ion battery, potassium ion battery, microwave absorption performance, dye removal, metal ion removal, and pesticide, herbicide removal.

A recent trend in carbon supercapacitor electrodes has seen the use of biomass waste materials to produce activated carbons. Supercapacitors with carbon electrodes derived from biomass materials such as European deciduous tree(Jain et al. 2021), poplar catkins

(Luo et al. 2021), celery (Ma et al. 2021), carbonized wood cell chamber (Xiong et al. 2021), Ficus religiosa (Senthilkumar and Selvan 2015), starch (Ghosh et al. 2019), honeyvine milkweed (Ariharan et al. 2021), carrot (Liu et al. 2020), pine saw dust (Quan, Su, and Gao 2020), chicken feather biopolymer (Wang et al. 2013) , Natural bamboo (Zhang et al. 2018), Pine cone (Bello et al. 2016), Clean corncobs (Xu et al. 2020) , Kapok fibers (Zhang et al. 2021), tree bark (Momodu et al. 2017)and Tremella (white fungus) (Guo et al. 2017) have been reported.

Literature survey

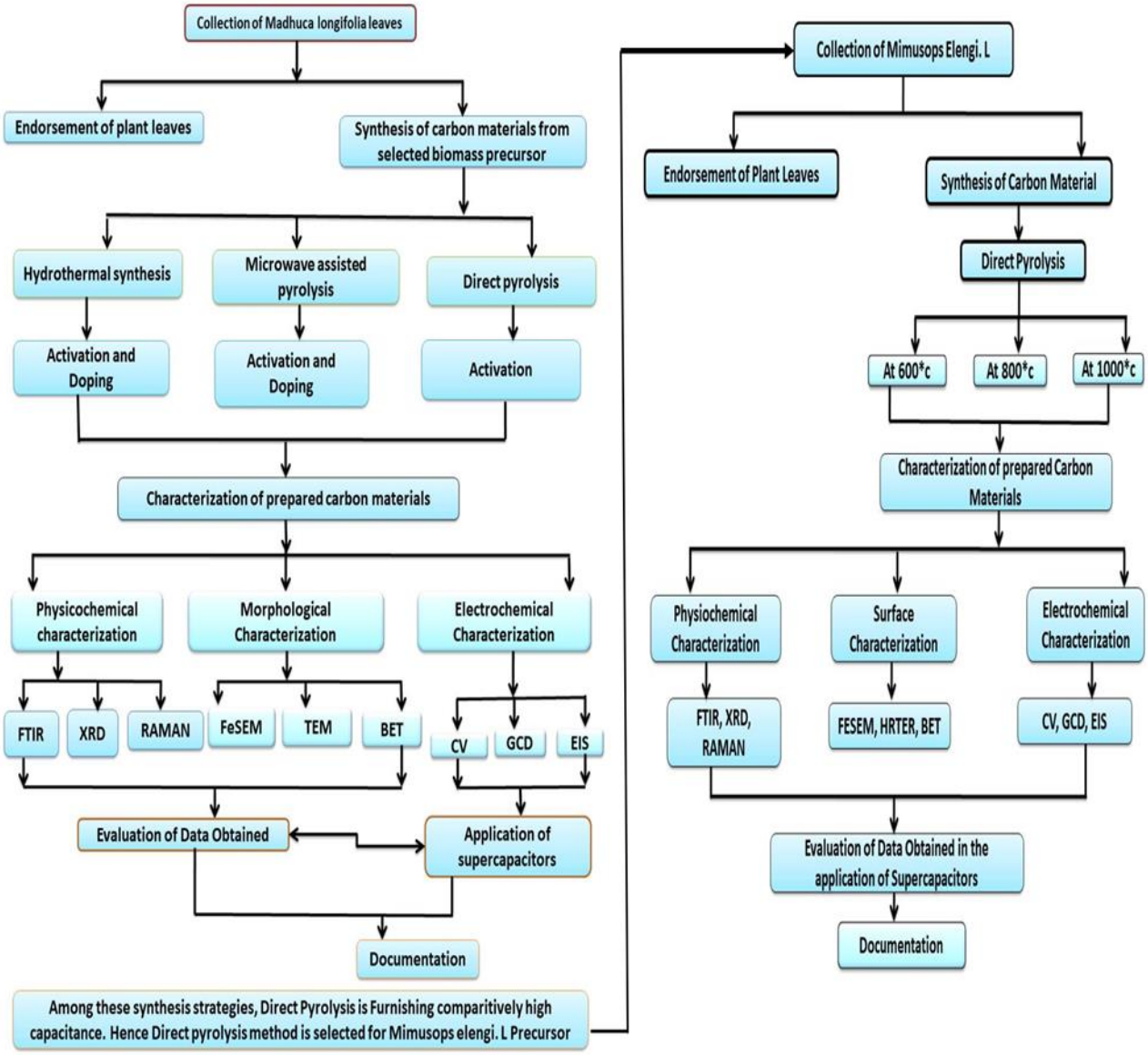
Review of Literature related to biomass-derived carbon materials by using plant leaves in the application of supercapacitors are carried out using various article data. (Shanmuga Priya, Divya, and Rajalakshmi 2020) Based on the literature survey, so far no research work is carried out using *Madhuca longifolia* (L.)J.F.Macbr and *Mimusops elengi L.* as precursors for the synthesis of carbon materials for supercapacitor applications.

Objectives

The research work aims to arrive facile synthetic strategy for the synthesis of carbon materials from zero cost environmentally friendly biomass precursors. The prime objectives of the research work are focused on the following

1. To synthesize biocarbon materials from selected eco-friendly biomass waste precursor *Madhuca longifolia* (ML) leaves using direct pyrolysis technique, hydrothermal carbonization technique (HTC) and microwave pyrolysis technique.
2. To synthesize biocarbon materials from selected *Mimuspos elengi* (ME) leaves using economically viable one step direct pyrolysis without any chemical activation.
3. To characterize the synthesized biocarbon material from leaves of *Madhuca longifolia* and *Mimuspos elengi* by structural characterization (FT-IR, XRD, Raman), morphological characterization (FESEM, HRTEM and BET) and electrochemical characterization (CV, GCD and EIS)
4. To derive carbon electrodes from selected green waste precursors and to evaluate the electrochemical performance of the bio carbon electrodes in energy storage supercapacitors.

Experimental framework



Methodology

The present investigation is carried out in four phases

Phase – I: Synthesis of carbon materials from *Madhuca longifolia* ((ML) and *Mimusops elengi* (ME)

Phase – II: Physiochemical characterization of synthesized carbon material from ML and ME leaves

Phase – III: Electrochemical and morphological characterization of ML and ME derived carbon materials

Phase – IV: Efficacy of synthesized carbon materials as supercapacitor electrodes

Phase – I: Synthesis of carbon materials from *Madhuca longifolia* leaves

Hydrothermal carbonization of *Madhuca longifolia* leaves

5 g of dried Madhuca longifolia leaves is mixed with KOH as activating agent in the ratio 3:1. The mixture is subjected to hydrothermal carbonization at 180ºC for 4 h. The obtained activated carbon is acid washed, dried at 90ºC for 12h and labelled as HTC-MLAC. For the introduction of hetero atom, urea has been used as dopant and the HTC-MLAC is carbonized with urea in the mass ratio 2:1 and the obtained material is washed, dried and finally labelled as HTC-MLNAC. (Sevilla and Fuertes 2009)

Microwave pyrolysis of *Madhuca longifolia* leaves extract

ML plant extract is prepared by dissolving 50g of ML powder in 250ml of DI water and heating it for 3 hours at 60ºC. The aqueous extract is filtered and stored in the refrigerator for further experiments. Then, 50 ml of the plant extract is subjected to microwave radiation for 6 mins at 700 W. The dark colour changing into reddish-black indicates the process of carbonization taking place inside the extract. After that, it is centrifuged at 5000 rpm for half an hour, and the filtrate is freeze-dried to get the solid product, which is named as ML derived Carbon (MLC). (Calvo et al. 2013)

Preparation of MnO_2 using co-precipitation method

0.22 mole/litre $MnSO_4$ is sonicated for 30 minutes in ultrasonic bath. 0.23 g of $KMnO_4$ has added to this mixture slowly under reflux conditions. The reaction is maintained in acidic conditions by adding acetic acid. The pH of the above mixture is maintained approximately 1. The reflux has carried out for 3 hours at 80ºC. After cooling to the room temperature, the sediments of the mixture are washed with DI water till the suspension becomes neutral. Then the neural suspension has filtered and the final black precipitate is dried at 60ºC for 18 hours. The obtained product is names as MnO_2. (Rao et al. 2019)

Fabrication of MLC/MnO_2

5 wt %, 10 wt %, 15 wt %, and 20wt % of MLC/MnO_2 are prepared by ultrasonic treatment. 4 g of ML derived carbon material is dissolved in 20ml of absolute ethanol under continuous stirring. 40mg of MnO_2 is added the above suspension and subjected to ultrasonic vibration for 2 hours. The resultant black precipitate MLC/MnO_2 – 10 is dried at 80ºC for 12

hours. Similarly, 5 wt %, 15 wt % and 20 wt % of MLC/MnO_2 are prepared and they are denoted as MLC/MnO_2 – 5, MLC/MnO_2 – 15 and MLC/MnO_2 – 20. (Rao et al. 2019)

Direct pyrolysis of *Madhuca longifolia*

10 g of dried powdered leaves of *Madhuca longifolia* are heated at the temperature of 600ºC, 800ºC and 1000ºC in alumina crucible for five hours in argon atmosphere in the tubular furnace. The resultant black solid is then washed with 5M HCl and dried overnight at 60ºC. The carbonized materials obtained from 600ºC, 800ºC and 1000ºC are denoted as MLC-600, MLC-800 and MLC-1000. (Biswal et al. 2013)

Chemical activation and doping of MLC

The carbonized sample at 800ºC is subjected to chemical activation using KOH as activator in the mass ratio 1:3. The carbon material and the activator is subjected to pyrolysis under inert Ar atmosphere for five hours at 800ºC. The obtained activated carbon material is then washed with 5M HCl and washed with DI water till the supernatant become neutral pH. Then the obtained mass is dried in oven for 12h at 60ºC. The sample obtained is named as MLAC. (Karnan et al. 2016)

Synthesis of carbon materials from *Mimusops elengi*

10 g of dried powdered leaves *Mimusops elengi* are heated at the temperature of 600ºC, 800ºC and 1000ºC in alumina crucible for five hours in argon atmosphere in the tubular furnace. The resultant black solid is then washed with 5M HCl and dried overnight at 60ºC. The carbonized materials obtained from 600ºC, 800ºC and 1000ºC are denoted as MEC-600, MEC-800 and MEC-1000. (Biswal et al. 2013)

Phase – II: Physiochemical characterization of synthesized carbon material from ML and ME leaves

The physicochemical characteristics of the synthesized pyrolyzed carbon material and their corresponding functionalized carbon material are characterized using Perkin Elmer FT-IR spectrophotometer with the SOFTWARE – OPUS version 6.5, ULTIMA IV Model X-ray Diffractometer with CuKα radiation (α = 1.5406 Å) in the range of 10–90° with count time (0.2 s) at 0.02 steps and Confocal Raman Microscope with AFM imaging (WiTec alpha 300, Germany)

- XRD patterns of the prepared carbon materials by direct pyrolysis technique reveals the amorphous nature of MLC-600, MLC-800, MLC-1000, MLAC, MEC-600, MEC-

800 and MEC-1000 prepared. Carbon materials synthesized from HTC technique and microwave pyrolysis i.e., HTC-MLAC, HTC-MLNAC, MLC/MnO_2-5, MLC/MnO_2-10, MLC/MnO_2-15 and MLC/MnO_2-20 reveals crystalline nature.

- FT-IR spectrum of all synthesized carbon materials for both precursors highlights the presence of OH, C=O, C-O functional groups on the surface. It represents the presence of carbon and oxygen rich functional groups in the prepared activated carbon matrix.
- Raman spectra of the prepared carbon materials confirms the typical D and G band around 1350 Cm^{-1} and 1590 cm^{-1}. The observed ID/IG ratio below 1 confirms the low degree of graphitization in the prepared ML and ME derived carbon materials.
- EDS analysis confirms the major elemental composition present in the synthesized carbon materials. The major amount of carbon and oxygen in the prepared materials are on par with FT-IR studies. There is also accountable nitrogen and trace amount of metals like Mg, Mn, Fe, Si and Cu in the prepared carbonaceous materials.

Phase – III: Electrochemical and morphological characterization of ML and ME derived carbon materials

To investigate the electrochemical properties of the synthesized functional carbon electrode materials by using active materials, Super-P as carbon conductive additive and polytetra-fluoroethylene (PTFE) as a binder in a weight ratio of 80:15:5 dissolved in NMP solvent. After ensuring well dispersion, the slurry is coated on graphite sheet with the surface area of $1cm^2$.The coated slurry are dried in hot vacuum oven at 100 °C for 24 h for solvent evaporation. 1 M H_2SO_4 used as the electrolyte in three electrode system. For three electrode configurations, synthesized carbon electrode active material of ML derived carbon and MLC/MnO_2 - x , saturated calomel electrode (SCE) and platinum used as a working electrode, reference electrode and counter electrode respectively. The prepared functional carbon materials were tested by Cyclic Voltammetry (CV) and Galvanostatic Charge/Discharge (GCD) analysis by using CH Instrument, Model CHI608E, USA. The specific capacitance, energy density and power density were calculated using the following equations. (Karnan et al. 2016) (Biswal et al. 2013) The surface morphological nature of the carbon materials synthesized by various techniques are characterized by TESCAN MIRA3 XMU Field emission scanning electron microscope, Transmission electron microscopy (TEM, 120 kV, FEI Tecnai G2) and BET using Quantachrome Instruments of ASiQwin (Version.3).

- The electrochemical capacitive behaviour of the CV profiles reveals the occurrence of low pseudo-capacitive nature due to the presence of high oxygen content with major electrical double layer capacitance (EDLC) behaviour in the prepared carbon materials.
- From GCD measurements, as the current density increases from 0.5 A/g to 5 A/g, the specific capacitance decreases due to fast charging on the electrode. At low current density, specific capacitance is high because the micropores are not empty to the electrolyte ions.
- HTC-MLAC shows the specific capacitance of 119.90 F/g, MLC/MnO_2-20 infers specific capacitance of 172 F/g, MLC-800 gives173 F/g and MEC-800 furnishes the capacitance of 249 F/g. It is due to the nature of the biomass precursor materials.
- The EIS analysis infers the physical and chemical process occurring in the carbon materials. The low values of charge transfer resistance with semi-circle in the high frequency implies the low ionic conductivity of the prepared MLAC and MEC-800 carbon materials.
- The energy density and power density gives the information about energy storage systems and the ragone plot of ML and ME derived carbon implies the supercapacitive nature of the prepared electrode materials.
- The microporous structure of the synthesized MLAC and MEC-800 carbon materials are confirmed by FESEM images. This is due to pyrolytic carbonization under the Ar atmosphere which results in the formation of micro and mesopores in the surface of the produced carbon materials.
- The interconnected porous spherical morphology is clearly depicted in the TEM images of the MLAC and MEC-800 samples.
- The surface of the synthesized MLAC and MEC-800 materials are determined by BJH model of BET nitrogen adsorption-desorption isotherm. From the results, it is inferred the type IV curve with the presence of micro and mesopores which are in good agreement with TEM morphology.

Phase – IV

Efficacy of synthesized carbon materials as supercapacitor electrodes

- Performance evaluation of carbon materials prepared from ML and ME precursors infer MLC-MnO_2-20**,** MLAC and MEC-800 materials show greater capacitance compared to other carbon materials HTC-MLAC, HTC-MLNAC, MLC-MnO_2-5,

MLC-MnO_2-10, MLC-MnO_2-15, MLC-600, MLC-800, MLC-1000 and MLAC. Table 1 illustrates the compilation of data obtained by physiochemical and morphological studies.

Table 1. Compilations of data obtained by physiochemical and morphological studies

Precursors	**XRD**	**FT-IR**	**EDS (Carbon content %)**	**RAMAN**	**FESEM**	**TEM**	**BET**
MLC-MnO_2-20	Crystalline	O-H, C=O, C-O	51.7	Low degree of graphitization	well-developed interconnected porous networks	Mesoporous structure with pores	Type – IV isotherm with micro and mesopores
MLAC	Amorphous	O-H, C=O, C-O	68.48	Low degree of graphitization	Well-developed interconnected tubular rod structures	Intertwined spherical morphology	Type – IV isotherm with micro and mesopores
MEC-800	Amorphous	O-H, C=O, C-O	60.56	Low degree of graphitization	interlinked rod shape filaments	Small-sized pores in the carbon skeleton	Type – IV isotherm with micro and mesopores

- Comparison of electrochemical performance of carbon materials derived from selected ML and ME precursors highlights that MLC-MnO_2-20**,** MLAC and MEC-800 materials works very well compared to all other carbon materials. Table 2 highlights the electrochemical performance of prepared carbon materials.

Table 2. Compilations of data obtained by electrochemical studies

Precursors	**CV**	**GCD**	**EIS**
MLC-MnO_2-20	Major pseudocapacitance behaviour	172.31 F/g	Low R_s and R_{ct} values
MLAC	Major EDLC with minor pseudocapacitance behaviour	173.8 F/g	Low R_s and R_{ct} values of
MEC-800	Major EDLC with loss of pseudocapacitance behaviour	231.6 F/g	lower values of R_s and R_{ct}

- Electrochemical performance of various biomass based activated carbon reported in literature reveals the values of specific capacitance in the range of 150-400 F/g. In this present work, the studied precursors could also furnish the specific capacitance value in the same range. The specific capacitance values of MLC and MEC are found to be 216.6 F/g and 249.15 F/g. Hence our precursors functions in suitable fashion as reported in the literature.
- Commercially available activated carbon electrodes selected from literature afford specific capacitance in the range 90-250 F/g. The investigated precursor ML and ME also furnish specific capacitance in this range. Table 3 represents the performance of synthesized ML and ME derived carbon materials with commercially available carbon materials.

Table 3. Performance of ML and ME derived carbon materials with commercially available activated carbon materials

Carbon material	Specific capacitance (F/g)
Maxsorb (AC1)	203
Norit Super 50 (AC2)	119
M10	223
M14	228
M15 B	249
FU1	98
FU1A	126
MLC/MnO_2-20	172
MLC-800	173
MLAC	216
MEC-800	249

Conclusion

Functionalized carbon materials (HTC-MLAC, HTC-MLNAC, MLC/MnO_2-5, MLC/MnO_2-10, MLC/MnO_2-15, MLC/MnO_2-20, MLC-600, MLC-800, MLC-1000 and MLAC) are successfully prepared from dried ***Madhuca longifolia*** *leaves* by hydrothermal carbonisation, Microwave pyrolysis and direct pyrolysis techniques. Functional carbon (MEC-600, MEC-800 and MEC-1000) is synthesised from ***Mimusops elengi*** leaves by direct pyrolysis technique. Characterization of all synthesized carbon materials reveal the selected precursor ML and ME can be considered as suitable candidates for supercapacitor electrodes. It can be concluded that the selected precursors could furnish supercapacitive nature of the synthesized carbon electrode materials for supercapacitors.

Publications

1. M. Shanmuga Priya , P. Divya, and R. Rajalakshmi (2020) A Review Status on Characterization and Electrochemical Behavior of Biomass Derived Carbon Materials for Energy Storage Supercapacitors in Journal of Sustainable Chemistry and Pharmacy, 16, 100243 DOI address: https://doi.org/10.1016/j.scp.2020.100243
2. M. Shanmuga Priya and R. Rajalakshmi (2023) Comparison of Porous Carbon Electrodes Derived from *Madhuca longifolia* Leaves by Hydrothermal Technique and Direct Pyrolysis Techniques Asian Journal of Chemistry, 35(4), 1037-1043 DOI: https://doi.org/10.14233/ajchem.2023.27597
3. M. Shanmuga Priya, N. Rudra and R. Rajalakshmi (2022) Green Eco-Friendly One-Pot Synthesis Of Luminescent Carbon Dots From Fruit Pod Of *Borassus Flabellifer* And Stem Of *Trigonella Foenum-Graecum L* And Its Anti-Microbial Applications, ECS transactions, 107 (1) 7759-7769 DOI address : 10.1149/10701.7759ecst

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